In Situ Polysulfide Detection in Lithium Sulfur Batteries

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Outline

- Background
  - Modified cathodes
  - Modified separators
- Approach
  - 4 electrode cell design
- Cyclic voltammetry results
  - Sulfur baseline
  - Modified cathodes
  - Modified separators
- Conclusions
- Future work

Polysulfide species during discharge

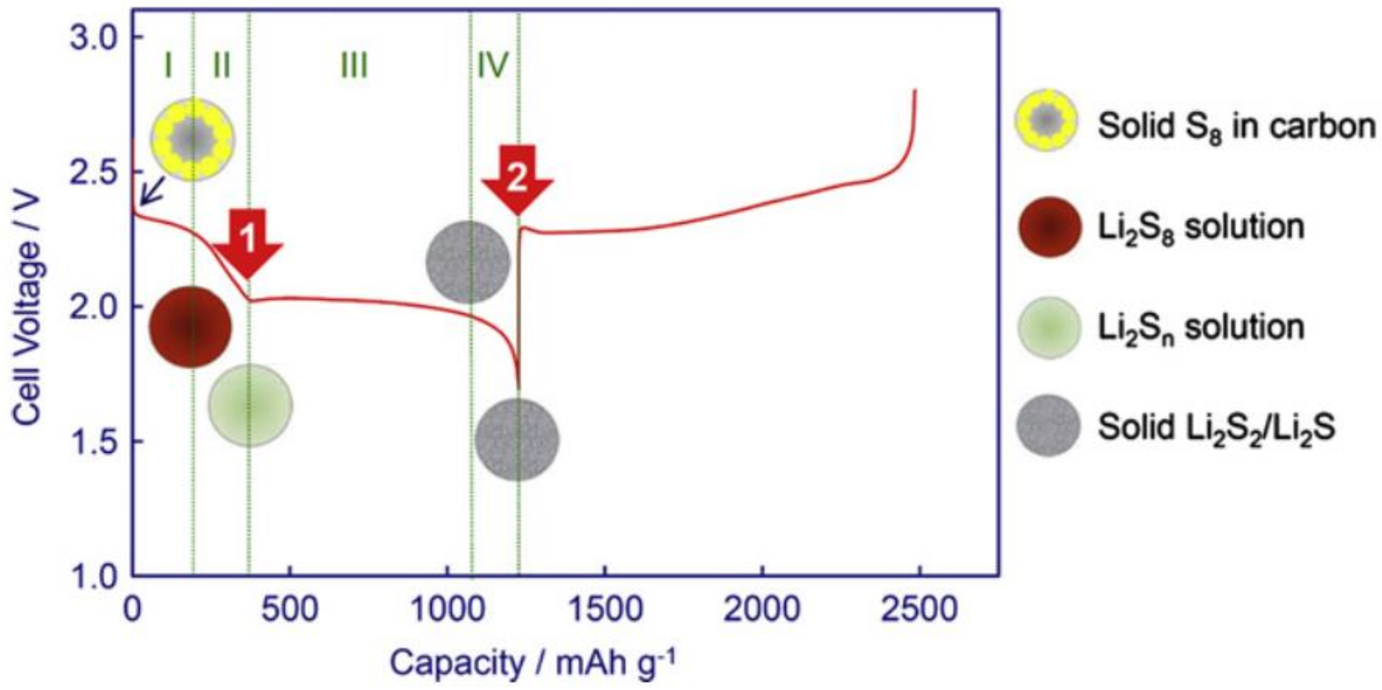
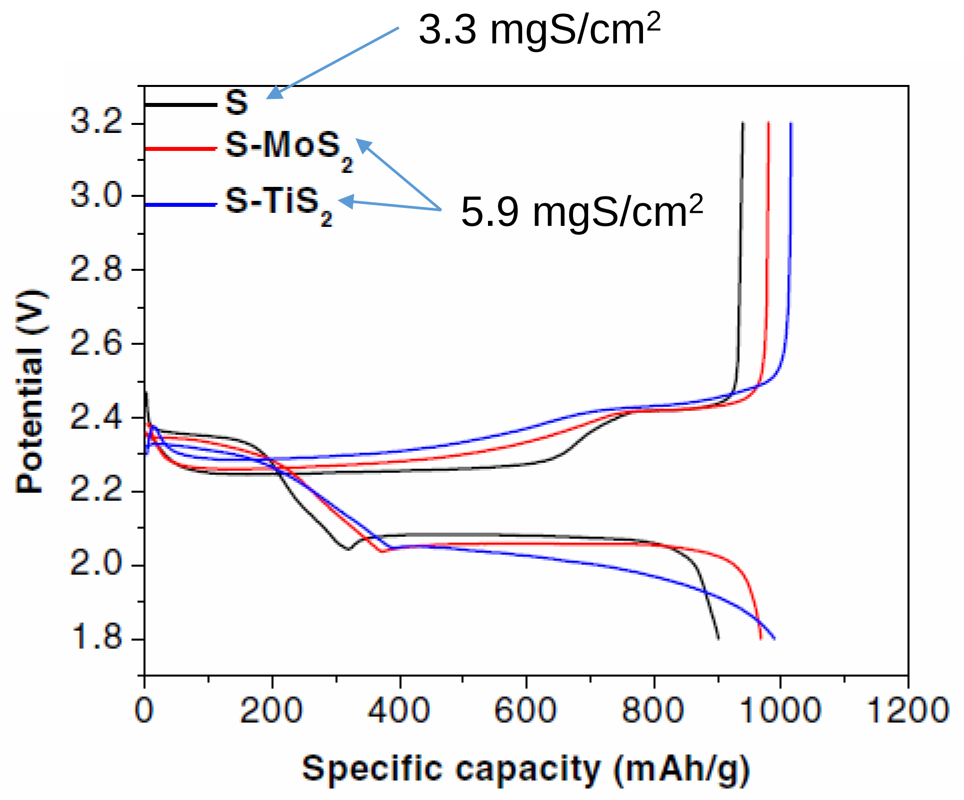


Fig. 1. A typical discharge and charge voltage profile of the first cycle of Li/S cells.

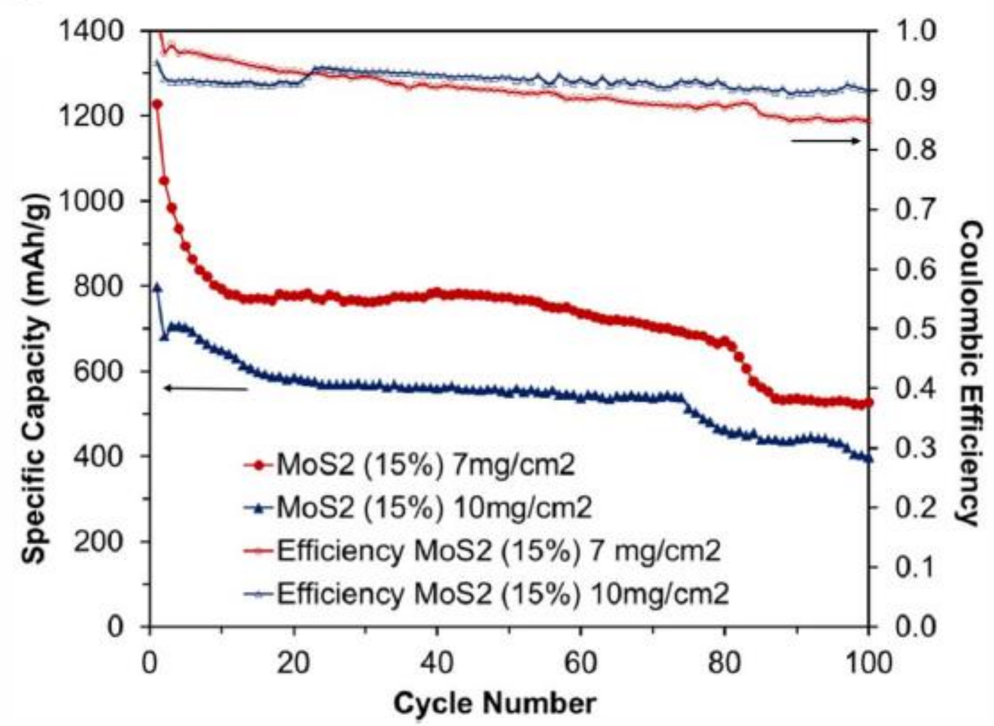
S.S. Zhang, *J. Power Sources.* 231 (**2013**) 153–162.
doi:10.1016/j.jpowsour.2012.12.102

- Intermediate discharge products (polysulfide species) are soluble in most organic electrolyte systems
- Polysulfide species can react with anode
- Essential to extract full capacity from cathode

Previous work with high loading metal sulfide blended cathodes

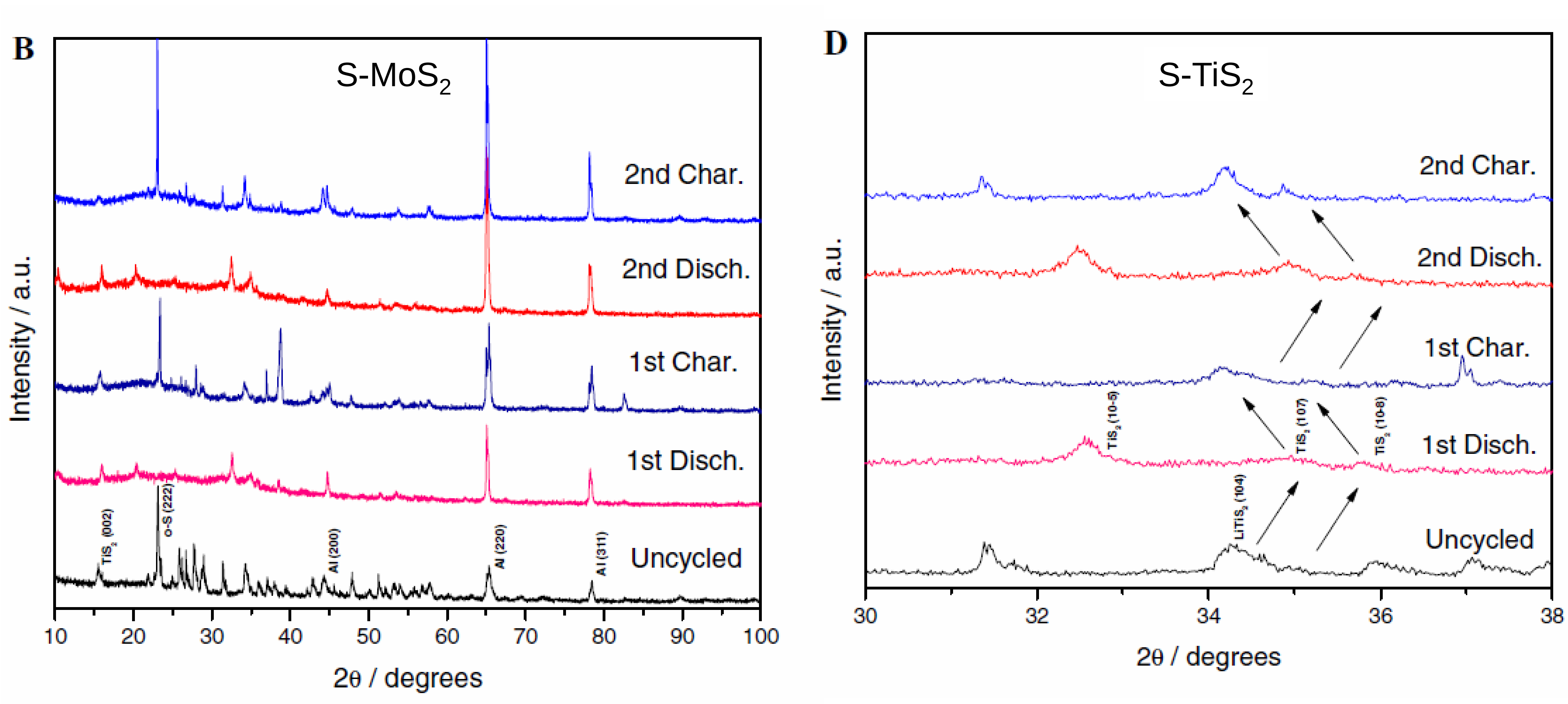


Replacing some carbon black with MoS_2 or TiS_2 allowed increased cathode loading while maintaining high capacity and stable performance over time



R. V. Bugga et al., *J. Electrochem. Soc.* 164 (**2017**) A265–A276. doi:10.1149/2.0941702jes

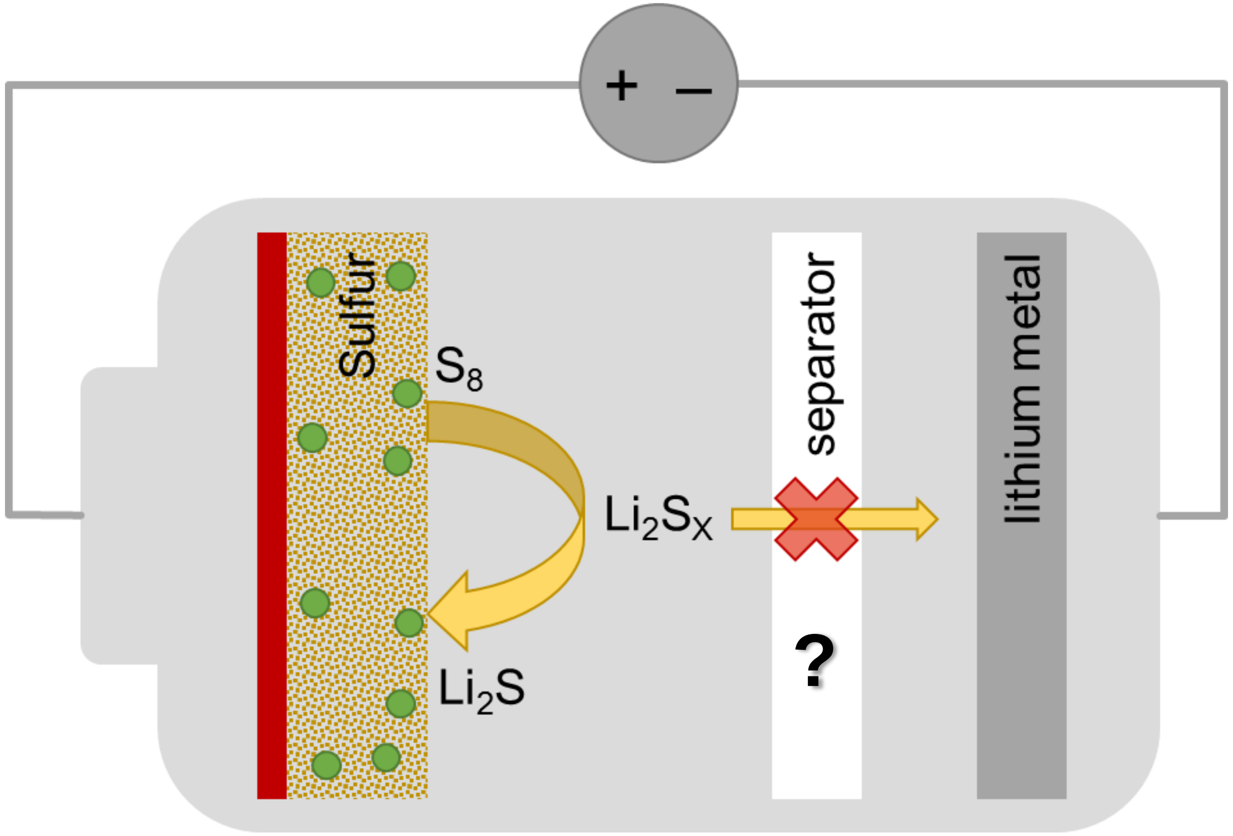
TiS_2 participates in cathode reactions, but MoS_2 doesn't by XRD analysis



R. V. Bugga et al., *J. Electrochem. Soc.* 164 (**2017**) A265–A276. doi:10.1149/2.0941702jes

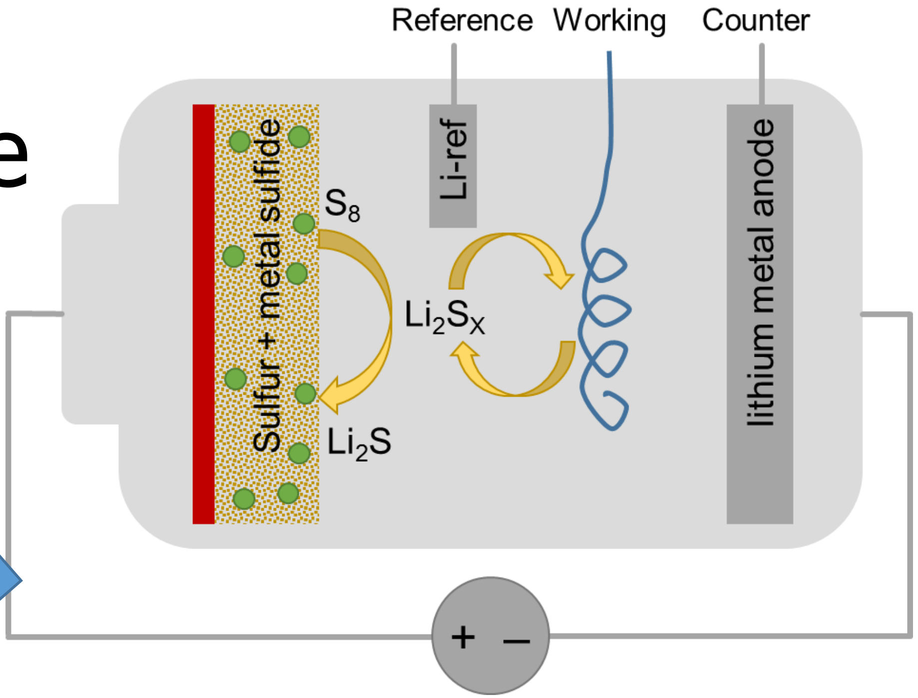
Separators also play major role in Li/S performance

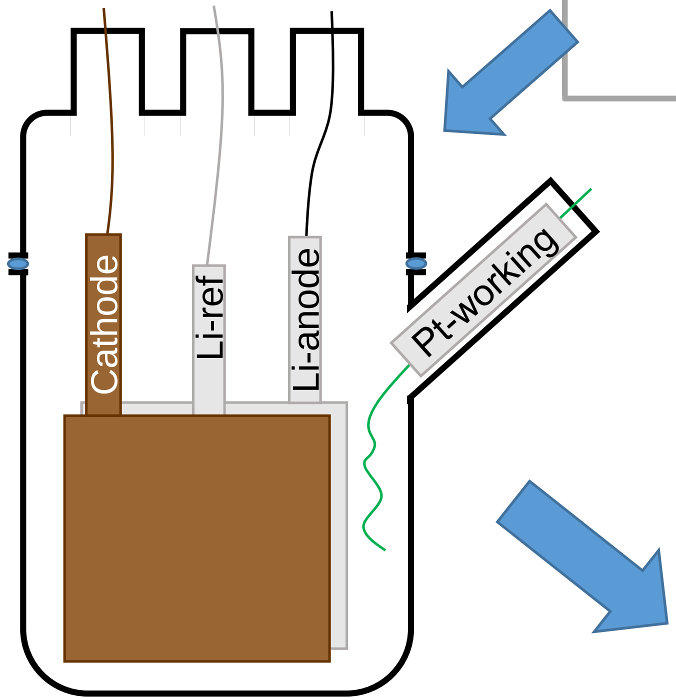
- Hypothesis that MoS_2 doesn't participate electrochemically motivated study on ceramic additives to separator
- Significant effects on discharge capacity and cycle life
- **Are the ceramic particles chemically interacting with dissolved polysulfide species?**



R. Bugga et al., *J. Electrochem. Soc.* 165 (**2018**) A6021–A6028. doi:10.1149/2.0051801jes

4-Electrode cell design

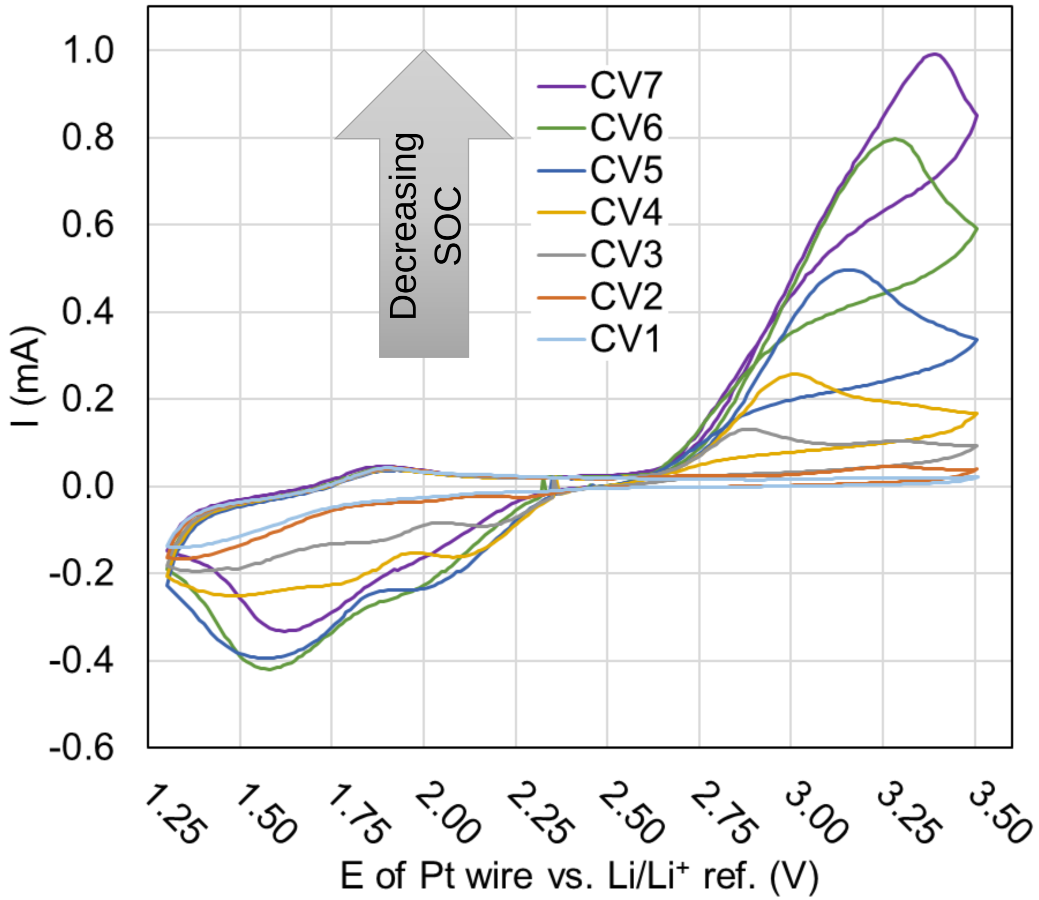




- Li/S prismatic cell with Li-metal reference and Pt wire working
- Li anode (2.5 x 2.5 cm), S cathode (2.5 x 2.5 cm) and Li ref. (0.5 x 1.0 cm) individually separated
- 6.35 mm (¼”) thick PE shim provides stack pressure and reduces electrolyte volume
- Pt wire with heat shrink tubing to isolate 0.8 cm^2 area
- Allows independent control of Pt wire in reference to Li-metal reference
- Li-anode used as counter
- 3 mL electrolyte volume

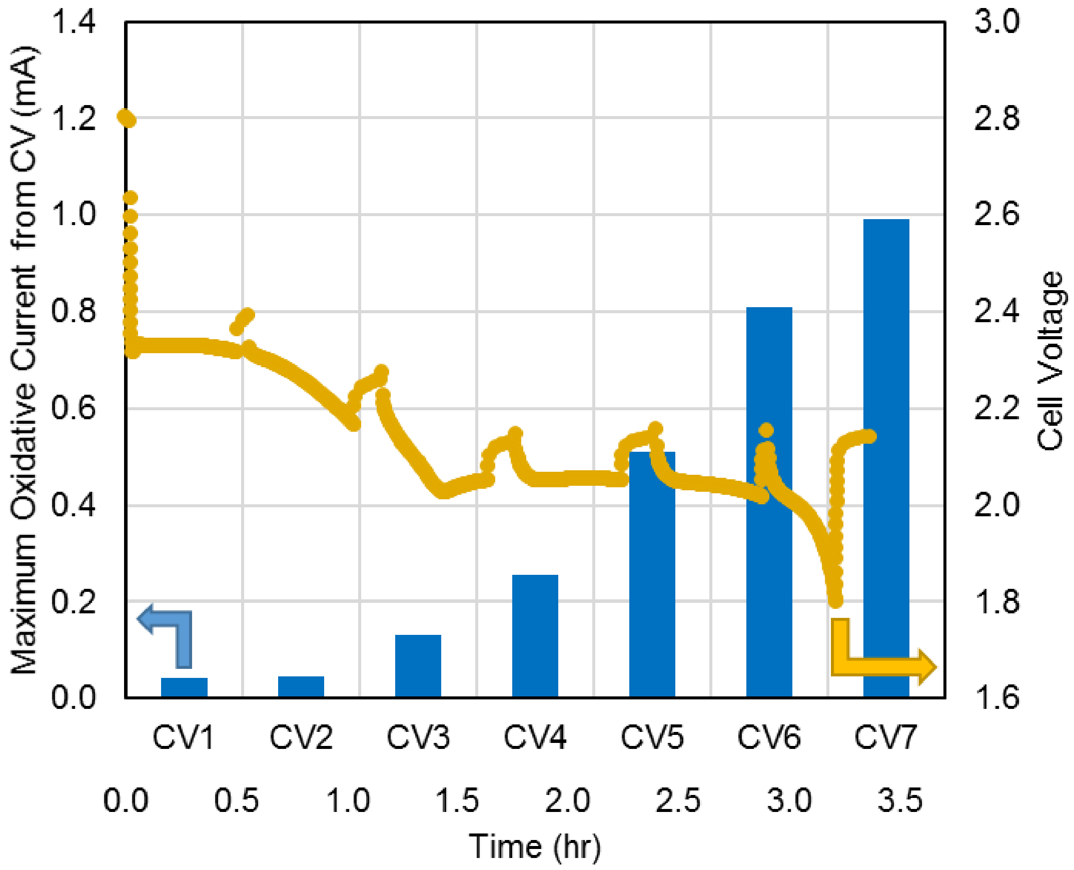
CV on Pt wire at stages during 1st discharge

- Standard sulfur cell
  - 3.6 mg/cm^2 S content
  - Tonen-Setela 20 μm separator
  - 3 mL 1.0 M LiTFSI DME+DOL (95:5 vol.) + 0.2 M $LiNO_3$
- Discharged at 0.75 mA/cm^2 (4.7 mA)
- Discharge paused every 10 % of theoretical capacity (2.23 mAh, based on 1000 mAh/g sulfur cathode)
- CV scan at 10 mV/s from OCV to 3.5 V, down to 1.3 V and back to OCV twice
- CV1 is initial scan
- CV7 is after 1.8 V cutoff voltage reached
- Reductive peak at ~1.4 V may be due to $LiNO_3$[1]



[1]Zhang, S. S. *Electrochim. Acta* **2012**, *70*, 344

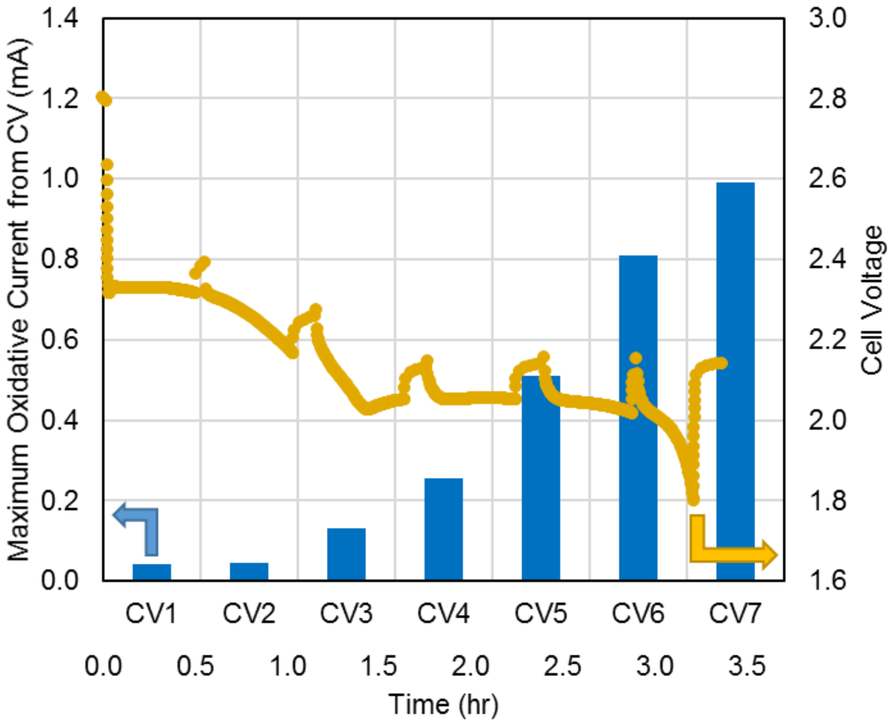
Discharge profile and maximum current in oxidative sweep



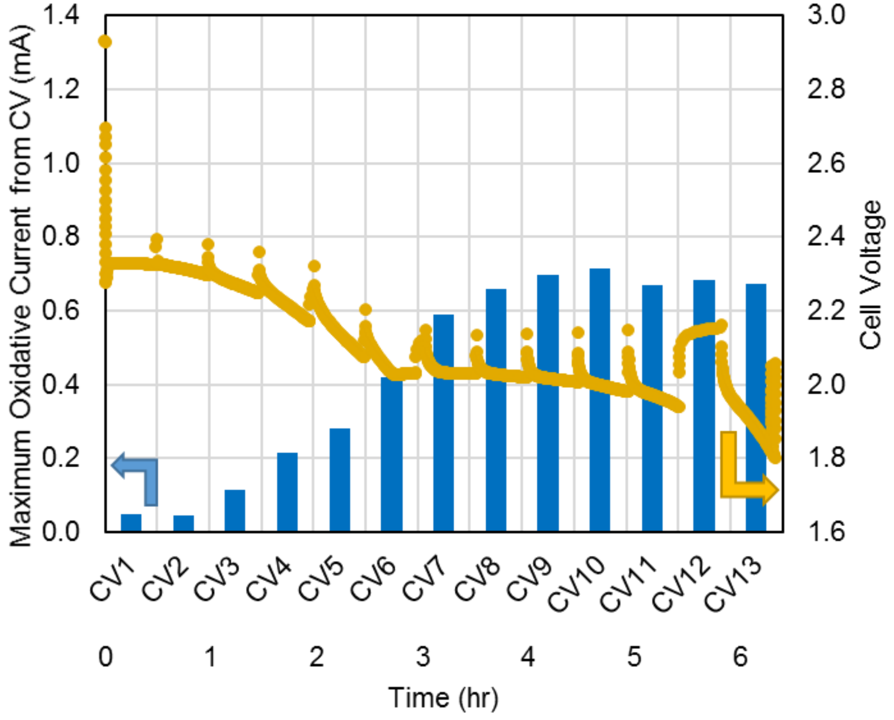
- Maximum current taken from CV
- Oxidizing S_X^{2-} species likely more repeatable than reducing oxidized product
- Full peak not resolved → difficult to integrate
- Peak height correlates with state of charge for first discharge

Comparison with Sulfur-MoS_2 composite cathode

Standard sulfur cathode with Tonen-Setela separator



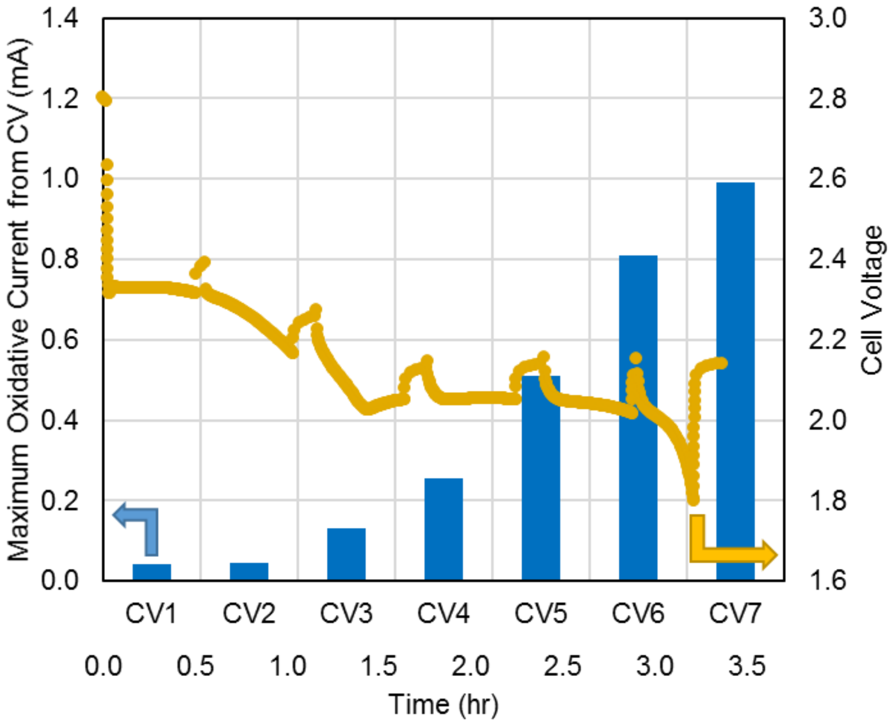
Sulfur-MoS_2 cathode* with Tonen-Setela separator



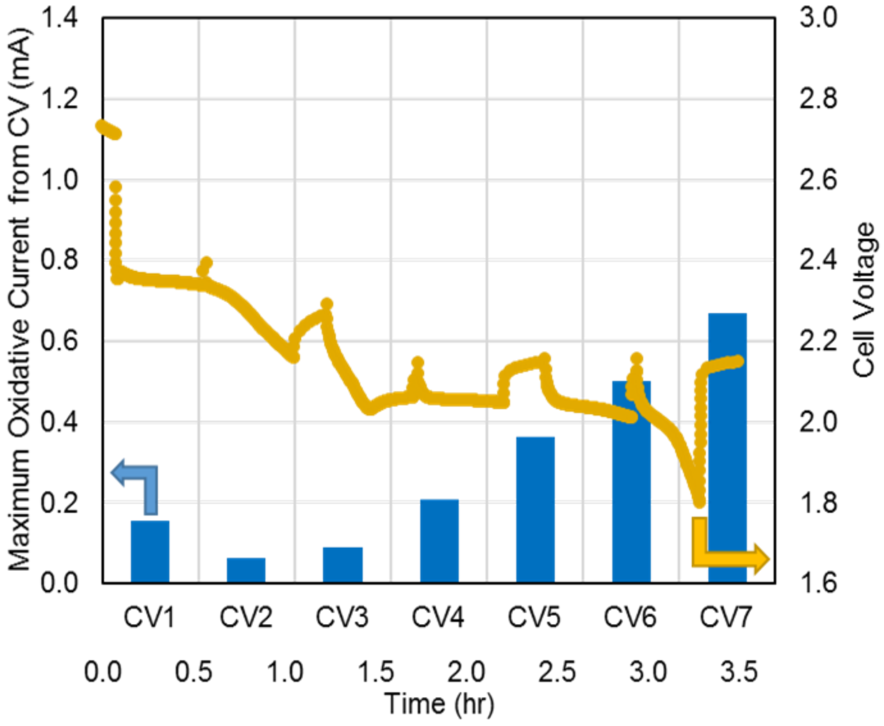
*capacity steps not adjusted for higher loading cathode

Comparison with ceramic Al_2O_3-coated separator

Standard sulfur cathode with Tonen-Setela separator

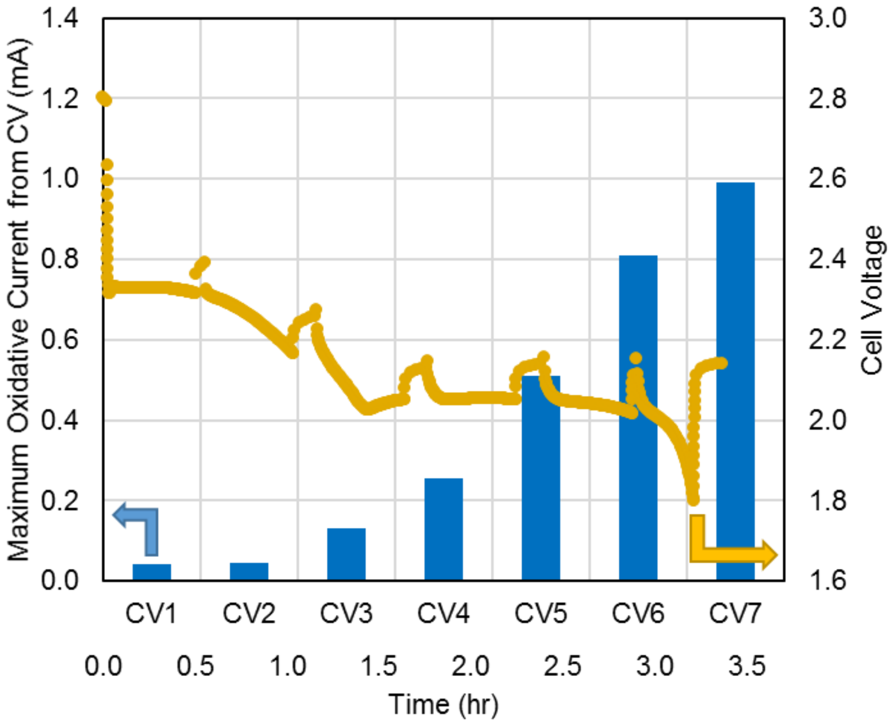


Standard sulfur cathode with Asahi Al_2O_3-coated separator

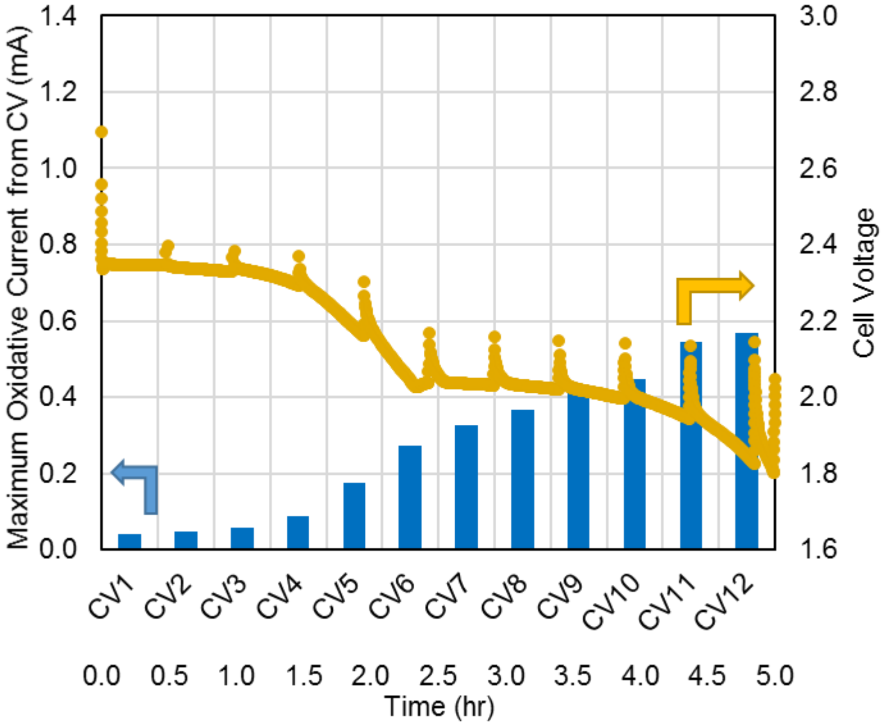


Comparison with sulfur-MoS_2 cathode and ceramic Al_2O_3-coated separator

Standard sulfur cathode with Tonen-Setela separator



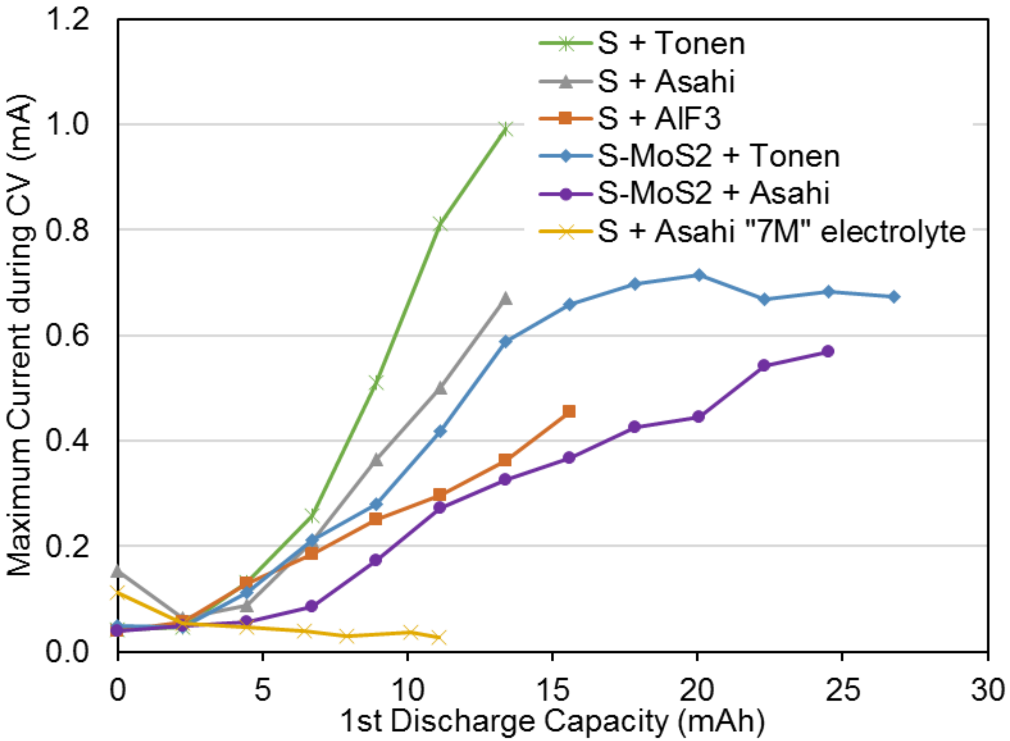
Sulfur-MoS_2 cathode* with Asahi Al_2O_3-coated separator



*capacity steps not adjusted for higher loading cathode

Maximum oxidative current comparison

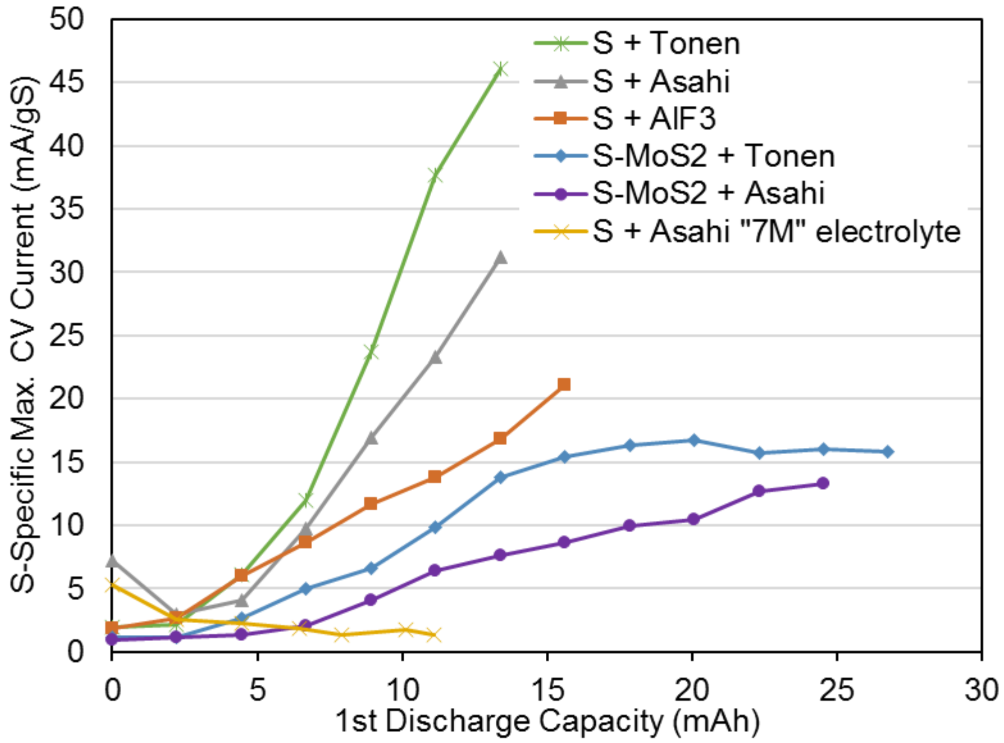
- Baseline sulfur cathode with Tonen separator produces highest concentration of sulfide species in short time
- Adding either Al_2O_3 or AlF_3 to separator reduces polysulfide species in electrolyte
- Adding MoS_2 to cathode reduces polysulfide concentration
- Adding both MoS_2 to cathode and Al_2O_3 to separator slows polysulfide migration
- Concentrated “7M” LiTFSI in DME+DOL (50:50)[1] virtually eliminates polysulfide content in electrolyte



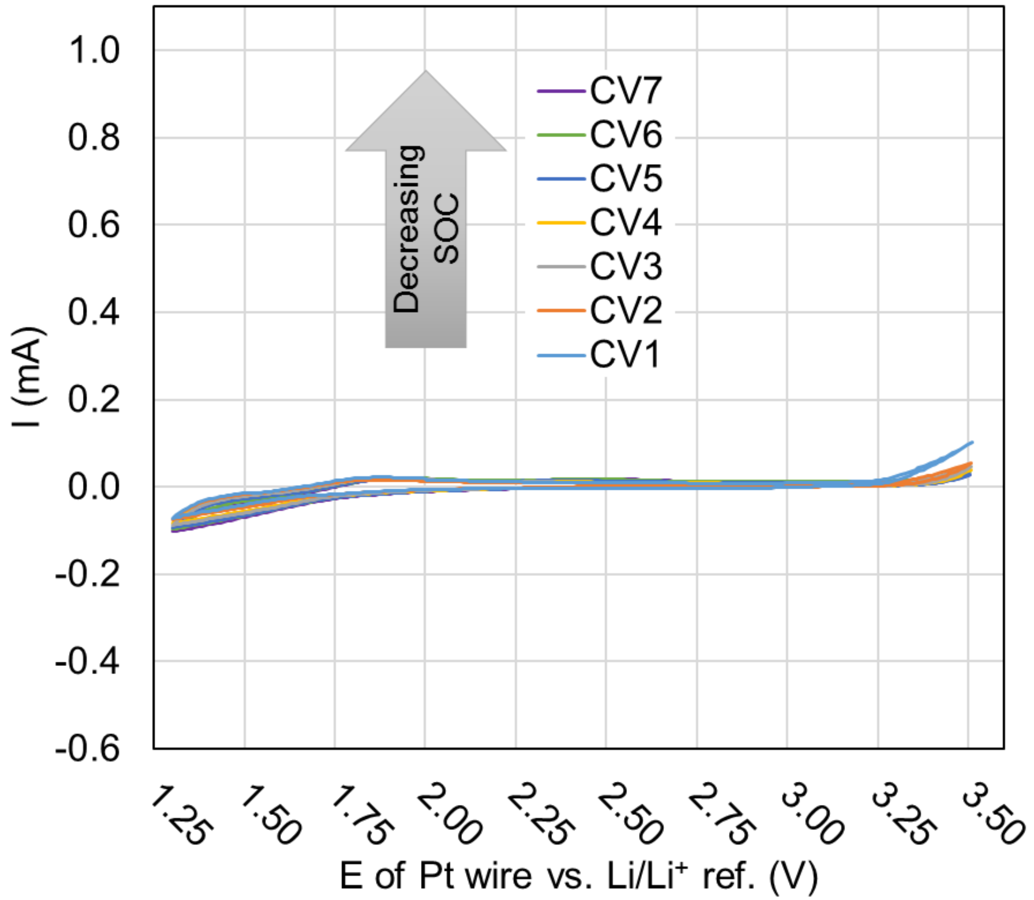
[1]L. Suo et al., *Nat. Commun.* 4 (**2013**) 1481. doi:10.1038/ncomms2513

Sulfur-specific maximum oxidative current comparison

- Plotted per gram of sulfur in cathode
- MoS_2-containing cathodes produce significantly lower polysulfide concentrations on a specific basis than pure sulfur cathodes



CV scans in concentrated electrolyte



- "7M" LiTFSI in DME+DOL (1:1) electrolyte
- Cell operated at 40 °C
- Sulfur cathode
- Tonen separator
- No appreciable sulfur in electrolyte during discharge

Conclusions

- 4-electrode prismatic glass cell indicates that polysulfide species start to accumulate during 2nd stage of 1st discharge
- Modifications to cathode and/or separator can affect concentration of polysulfide species in electrolyte
    - Cell with MoS_2-modified cathode reached equilibrium condition during 2nd voltage plateau
- Although there is some reduction in soluble polysulfide species when modified cathode or separator are used, they have not been fully suppressed
    - Does not explain improved performance
- High concentration "7M" electrolyte showed no peak attributable to polysulfide species

Ongoing and Future Work

- Develop method to automate CV and discharge measurements
  - Increase number of CV scans during discharge
  - Run CV scans during charge
  - Decrease downtime for cell
- Develop better sealing technique to prolong cell life
  - Study effect of cycling on polysulfide concentration
- Apply method to new cathode/separator modifications
- Investigate cause for improved capacity and cycle life from modified cathodes and separators

Acknowledgements

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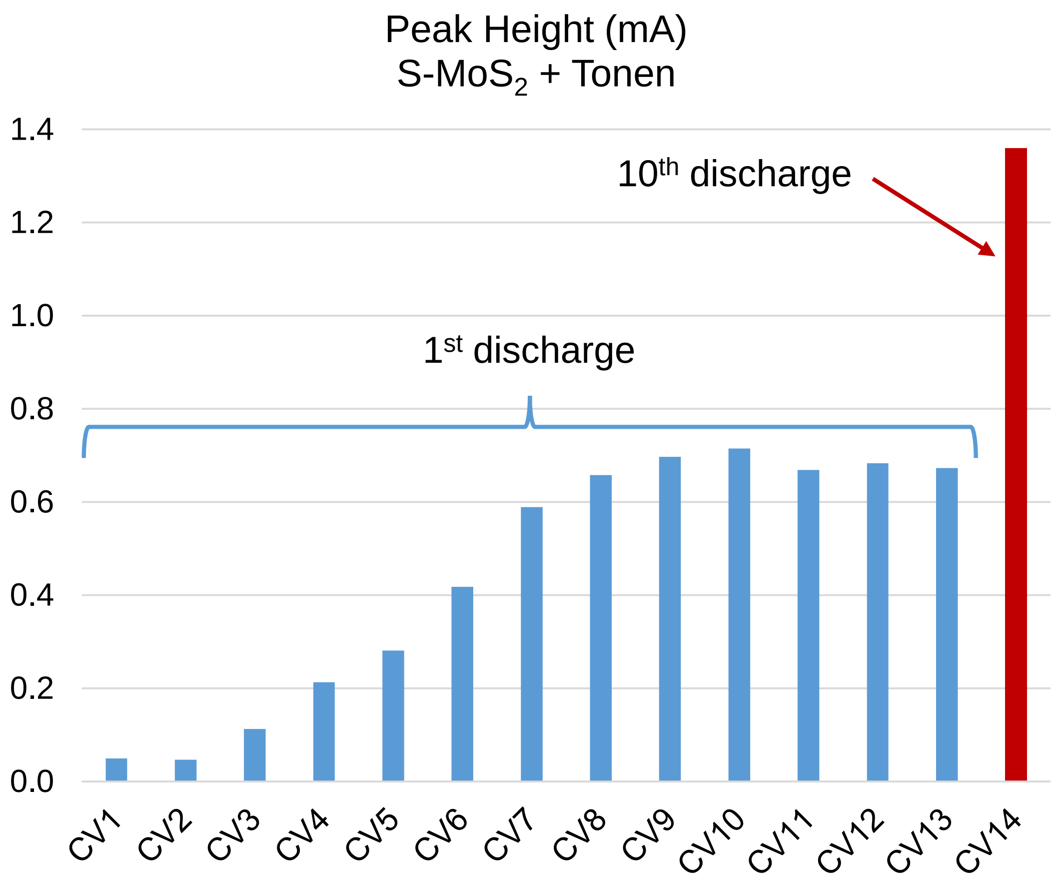
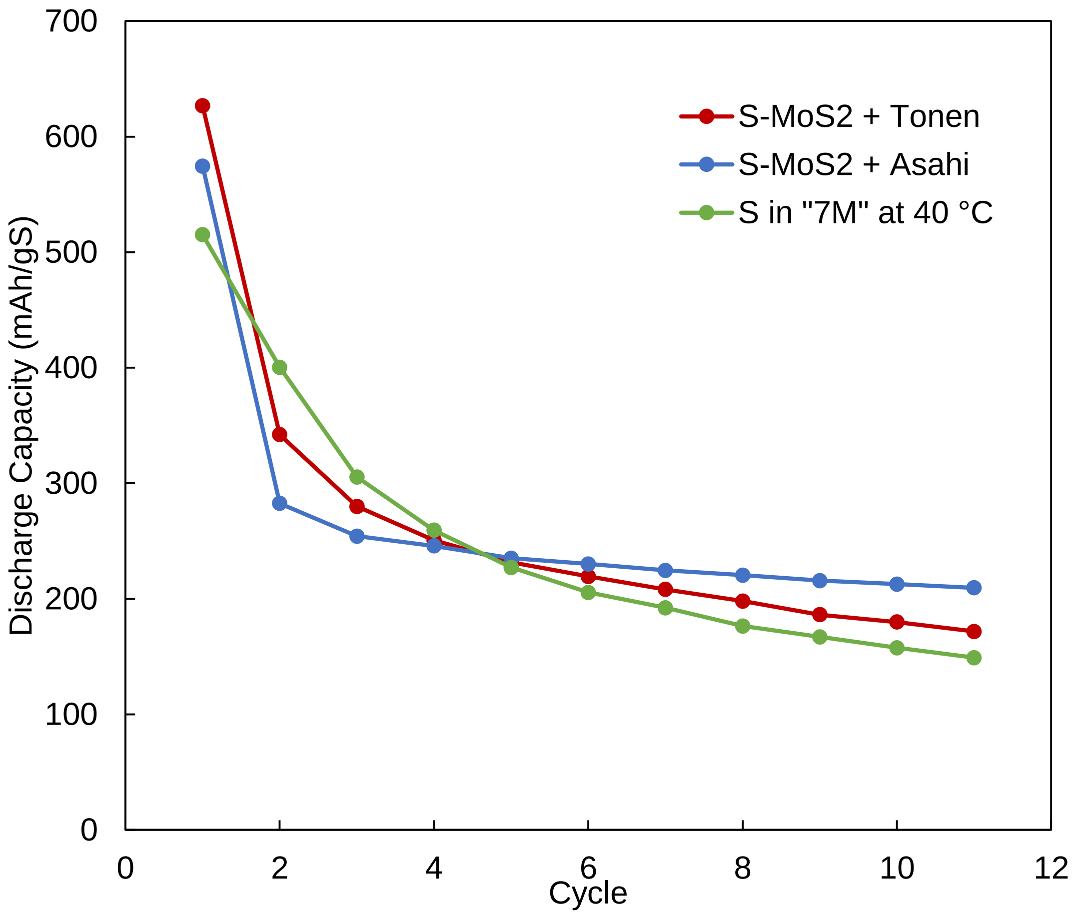
Backup

Growth of sulfide peak after cycling



- Sulfide concentration grows with cycling in the case of S-MoS$_2$
- Increases to approximately same level as pure sulfur cathode with Tonen after 10 cycles
- Indicates that sulfide species eventually make it into electrolyte

Rapid capacity fade after first cycle



- Unclear if sharp drop in capacity is due to CV studies or cell design
- Sealing is not as good as coin cell